Formation and X-ray Structures of PCP Ligand Based Platinum(II) and Palladium(II) Macrocycles

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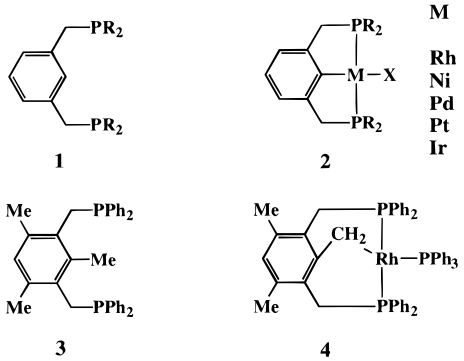
The coordination behavior prior to C−M bond formation of the chelating aromatic PCP substrate DPPMH (**3**; DPPMH = 1,3-bis((diphenylphosphino)methylene)mesitylene) has been studied in order to determine the factors which control the complex formation of such ligands. Reacting **3** with $(RCN)_2MCl_2$ (R = Me, Ph; M = Pd, Pt) and $(COD)PtX_2$ (X = Cl, Me; COD = 1,5-cyclooctadiene) resulted in the formation of several 8- and 16-membered mono- and binuclear palladium(II) and platinum(II) macrocycles: *trans*-$[(DPPMH)PdCl_2]_2$ (**5**), *trans*-$[(DPPMH)PtCl_2]_2$ (**6**), *cis*-$(DPPMH)PtCl_2$ (**7**), *cis*-$(DPPMH)PtMe_2$ (**8**), and *cis*-$[(DPPMH)PtMe_2]_2$ (**9**). Compounds **5**−**9** were fully characterized using NMR, FAB-MS, FD-MS, elemental analysis, and X-ray crystallography. Thermolysis of the bimetallic *trans*-$[(DPPMH)PtCl_2]_2$ (**6**) results in the formation of the monomeric *cis*-$(DPPMH)PtCl_2$ (**7**). The product formation depends on the neutral- (nitriles or COD) and anionic ligands (Cl and CH_3) of the metal precursor. The molecular structures of *trans*-$[(DPPMH)PdCl_2]_2$ (**5**) and *cis*-$[(DPPMH)PtMe_2]_2$ (**9**) have been determined by complete single-crystal diffraction studies. Crystal data for **5**: monoclinic, space group $P2_1/n$ with $a = 14.547(3)$ Å, $b = 17.431(4)$ Å, $c = 27.839$ (5) Å, $\beta = 99.56(2)°$, $V = 6961(3)$ Å^3, and $Z = 4$. The structure converged to $R = 0.048$ and $R_w = 0.049$. Crystal data for **9**: monoclinic, space group $P2_1/n$ with $a = 19.187(4)$ Å, $b = 19.189(4)$ Å $c = 20.705(2)$ Å, $\beta = 103.41(3)°$, $V = 7415(3)$ Å^3, and $Z = 4$. The structure refinement converged to $R = 0.0977$ and $R_w = 0.2212$.

Introduction

PCP-type ligands such as 1,3-$(R_2PCH_2)_2C_6H_4$ (**1**; R = aryl, alkyl) are known to react with various metal complexes to give bi-cyclometallated products **2** possessing two five-membered rings.[1] The cyclometallation reaction by which such complexes are formed is a widely occurring process used both in organometallic chemistry[1,2] and in organic synthesis.[3] PCP ligands such as 1,3-((diphenylphosphino)methylene)mesitylene (DPPMH; **3**) react with various rhodium precursors to give bi-cyclometallated products (e.g., **4**, $(DPPM)RhPPh_3$), possessing two six-membered rings, which are used in studies of the activation and functionalization of C−C bonds.[4]



A study of the coordination behavior prior to the C−M bond formation of the aromatic PCP substrates such as **1** and **3** has not been reported to our knowledge. We are interested in the factors which control the coordination chemistry of **3** with readily available palladium(II) and platinum(II) precursors such as $(RCN)_2MCl_2$ (R = Me, Ph; M = Pd(II), Pt(II)) and $(COD)PtX_2$ (COD = 1,5-cyclooctadiene; X = Cl, Me).[5,6] The COD and nitrile ligands are easily displaceable by phosphines to yield complexes of the type L_2MX_2.[5] In this paper we show that the coordination behavior of the PCP ligand (**3**), leading to the formation of mono- and dinuclear complexes, is controlled by the neutral (nitriles or olefins) and anionic ligands (Cl and CH_3) of the metal precursors.

Factors influencing the geometry, size, and shape of metal macrocycles are complex and are a subject of interest.[7,14,20] The majority of bimetallic, square planar, complexes possess two chelating ligands in a mutually *trans* configuration (type **A**);[8a] bimetallic, square planar complexes with two ligands in a *cis* arrangement are also known (type **B**).[8b] We are interested in

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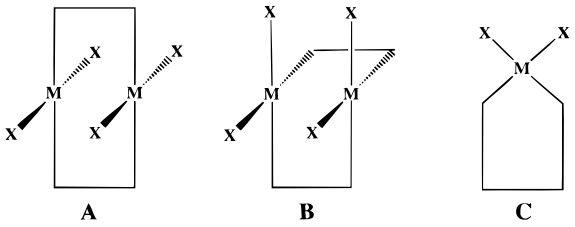
conditions leading to monomeric PCP complexes of type **C**. Such complexes of ligand **3** are attractive models for studying competitive C−H and C−C activation processes since one of the methyl groups is directed toward the metal center.[4]



We report on the formation and X-ray analysis of 16-membered binuclear palladium(II) and platinum(II) macrocycles (**5**, **6**, type **A**; **9**, type **B**) and 8-membered monometallic platinum(II) complexes (**7**, **8**, type **C**) using the DPPMH ligand (**3**).

Experimental Section

General Procedures. All reactions were carried out under nitrogen in a Vacuum Atmospheres glovebox (DC-882) equipped with a recirculation (MO-40) "Dri Train" or under argon using standard Schlenk techniques. Solvents were reagent grade or better, dried, distilled, and degassed before introduction into the glovebox, where they were stored over activated 3 Å molecular sieves. Deuterated solvents were purchased from Aldrich and were degassed and stored over 3 Å activated molecular sieves in the glovebox. $(RCN)_2MCl_2$ (R = Me, Ph; M = Pd, Pt), $(COD)PtX_2$ (COD = 1,5-cyclooctadiene; X = Cl, Me) and DPPMH (**3**) were prepared by published procedures[4−6,9,10] or obtained commercially. Reaction flasks were washed with water and acetone and oven-dried prior to use. Fast atom bombardment (FAB) and field desorption (FD) mass spectra were measured by the Institute of Mass Spectrometry at the University of Amsterdam, The Netherlands. Elemental analyses were carried out at the Hebrew University, Jerusalem, Israel.

Spectroscopic Analysis. The ^1H, ^{31}P, and ^{13}C NMR spectra were recorded at 400.19, 161.9, and 100.6 MHz respectively on a Bruker AMX 400 NMR spectrometer. All chemical shifts (δ) are reported in parts per million and coupling constants (J) in hertz. The ^1H and ^{13}C NMR chemical shifts are relative to tetramethylsilane; the resonance of the residual protons of the solvent was used as an internal standard h_1 (7.26 ppm chloroform) and all-d solvent peaks (77.0 ppm chloroform), respectively. $^{31}P\{^1H\}$ NMR chemical shifts are relative to 85% H_3PO_4 in D_2O at δ 0.0 (external reference), with shifts downfield of the reference considered positive. Assignments in the ^1H and $^{13}C\{^1H\}$ NMR were made using ^{13}C-DEPT-135 (distortionless enhancement by polarization transfer) and HMQC (heteronuclear multiple quantum correlation) experiments. All measurements were carried out at 298 K unless otherwise specified.

Synthesis of *trans*-[(DPPMH)PdCl$_2$]$_2$ (5). To a well-stirred suspension of 259 mg (1.0 mmol) of $(MeCN)_2PdCl_2$ (or $(PhCN)_2PdCl_2$) in 20 mL of tetrahydrofuran (THF) was added dropwise a solution of DPPMH (**3**; 516 mg, 1.0 mmol) in 10 mL THF at room temperature. After 12 h the yellow precipitate that had formed was filtered, washed with 3 × 20 mL of pentane, and dried in vacuo, to yield 675 mg (97%) of compound **5**, which is sparingly soluble in most organic solvents. Yellow crystals of **5** suitable for X-ray crystallography were obtained from chloroform. FAB-MS: 1387 $(m/e)^+$. Anal. Calcd for $C_{70}H_{68}Cl_4P_4Pd_2$ (%): C, 60.58; H, 4.94; Cl, 10.22. Found: C, 60.28; H, 5.24; Cl, 10.34. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.31 (s). ^1H NMR ($CDCl_3$): δ 7.8 (br s, 16 H, *o*-PAr*H*), 7.3 (br s, 24H, *m*,*p*-PAr*H*), 6.26 (s, 2 H, *p*-C$_6$*H*Pd), 3.81 (s, 8 H, CH_2P), 1.56 (s, 12 H, 4−6-(CH_3)$_2$C$_6$HPd), 1.24 (s, 6 H, 2-(CH_3)C$_6$HPd). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.8 (s, C_{ortho}−C$_6$HPd), 136.5 (s, C_{meta}−C$_6$HPd), 134.2 (br s, C_{Ar}), 130.3 (s, C_{Ar}), 129.9 (d, J_{PC} = 49.1 Hz), 128.3 (s, C_{Ar}), 127.9 (br s, C_{Ar}), 26.7 (vt, $^1J_{PC}$ = 10.4 Hz, *C*H$_2$P), 23.8 (s, 2-(*C*H$_3$)C$_6$HPd), 20.6 (s, 4−6-(*C*H$_3$)$_2$C$_6$HPd).

Synthesis of *trans*-[(DPPMH)PtCl$_2$]$_2$ (6). To a well-stirred suspension of 67 mg (0.19 mmol) of $(MeCN)_2PtCl_2$ (or $(PhCN)_2PtCl_2$) in 5 mL of CH_2Cl_2 (THF or benzene can be used as well) was added a solution of DPPMH (**3**; 100 mg; 0.19 mmol) in 5 mL of CH_2Cl_2, dropwise at room temperature. After 4 h the yellow solution was concentrated to approximately 1 mL, washed with 3 × 10 mL of cold pentane, and dried in vacuo to yield 142 mg (95%) of a white powder. FD-MS: 1566 $(m/e)^+$ Anal. Calcd for $C_{70}H_{68}Cl_4P_4Pt_2{\cdot}2CH_2Cl_2$ (%): C, 49.84; H, 4.18. Found: C, 49.05; H, 4.10. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.49 (s, $^1J_{Pt,P}$ = 2526 Hz). ^1H NMR ($CDCl_3$): δ 7.2−7.6 (m, 40 H, PAr*H*), 6.46 (s, 2 H, Ar*H*), 4.10 (s, 8 H, CH_2P), 1.91 (s, 12 H, 4−6-(CH_3)$_2$C$_6$HPt), 1.83 (s, 6 H, 2-(CH_3)C$_6$HPt). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.0−138.0 (m, br, C_{Ar}, not resolved), 26.3 (s, br, *C*H$_2$P), 21.6 (s, 2-(*C*H$_3$)C$_6$HPt), 19.0 (s, 4−6-(*C*H$_3$)$_2$C$_6$HPt).

Synthesis of *cis*-(DPPMH)PtCl$_2$ (7). To a well-stirred suspension of $(COD)PtCl_2$ (72 mg; 0.19 mmol) in 5 mL of CH_2Cl_2, was added a solution of DPPMH (**3**; 100 mg, 0.19 mmol) in 5 mL of CH_2Cl_2, dropwise at room temperature (THF or benzene can be used as well). After 4 h the light yellow solution was concentrated to 2 mL, washed with 4 × 10 mL of pentane, and dried in vacuo, to yield 142 mg (95%) of white *cis*-(DPPMH)PtCl$_2$. FD-MS**:** 748 [M^+ − Cl], FAB-MS: 710 [M^+ − 2Cl] Anal. Calcd for $C_{23}H_{41}Cl_1P_2Pt_1{\cdot}^1/_2THF$ (%): C, 46.47; H, 7.02. Found: C, 46.52; H, 6.81. $^{31}P\{^1H\}$ ($CDCl_3$): δ 7.67 (s, br, $^1J_{PPt}$ = 3739 Hz). ^1H ($CDCl_3$): δ 7.6−6.5 (20 H, m, br, P(C$_6$*H*$_5$)$_2$), 6.40 (1 H, s, br, *p*-H C$_6$H), 3.6−4.8 (4 H, m, br, CH_2P), 1.71 (6 H, s, br, 4,6-(CH_3)$_2$C$_6$H), 0.59 (3 H, s, br, 3 H, 2-(CH_3)C$_6$H). $^{13}C\{^1H\}$ ($CDCl_3$, 313 K): δ 139.5 (s, br, Ar), 137.2 (s, br, Ar), 134.0 (s, br, Ar), 130.3 (s, br, Ar), 128.8 (s, br, Ar), 127.3 (s, br, Ar), 34.5 (s, br, *C*H$_2$P), 21.6 (s, br, 4,-(*C*H$_3$)$_2$C$_6$H), 17.6 (s, br, 3,5-(*C*H$_3$)$_2$C$_6$H).

Synthesis of *cis*-(DPPMH)PtMe$_2$ (8). To a well-stirred solution of *cis*-(DPPMH)PtCl$_2$ (**7**; 100 mg; 0.13 mmol) in 10 mL of THF at −30 °C, was added dropwise a 5 mL solution of MeLi (0.30 mmol) in THF. The orange reaction mixture was allowed to warm to room temperature and was stirred for 30 min. The resulting suspension was filtered over a cottonpad, dried in vacuo, extracted with 3 × 20 mL of benzene, and dried again in vacuo to yield 85 mg (85%) of a white powder. Anal. Calcd for $C_{37}H_{40}P_2Pt_1$ (%): C, 59.91; H, 5.44. Found: C, 59.68; H, 5.60. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 14.47 (s, $^1J_{Pt,P}$ = 1842.4 Hz). ^1H NMR ($CDCl_3$): δ 6.5−8.0 (br m, 20 H, PAr*H*), 6.51 (br s, 1 H, Ar*H*), 3.70 (s, br, 4 H, CH_2P), 1.92 (s, br, 3 H, 2-(CH_3)$_2$C$_6$HPt), 1.44 (s, 6 H, 4−6-(CH_3)C$_6$HPt), 1.13 (s, br, 6 H, PtCH_3) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 128.0−138.0 (m, br, C_{Ar}, not resolved), 30.2 (s, br, *C*H$_2$P), 21.7 (s, br, 2-(*C*H$_3$)C$_6$HPt), 18.9 (s, br, 4−6-(*C*H$_3$)$_2$C$_6$HPt), 7.0 (d, br, $^2J_{PC,trans}$ = 98.4 Hz, $^1J_{PtC}$ = 623.6 Hz, Pt*C*H$_3$).

Synthesis of *cis*-(DPPMH)PtMe$_2$ (8) and *cis*-[(DPPMH)PtMe$_2$]$_2$ (9). To a stirred colorless solution of $(COD)PtMe_2$ (64 mg; 0.19 mmol) in 10 mL of benzene, was added dropwise a solution of DPPMH (**3**; 100 mg; 0.19 mmol). The reaction mixture was stirred overnight at room temperature (monitoring the reaction mixture in $CDCl_3$ by $^{31}P\{^1H\}$ NMR shows a mixture of **8** and **9**; ratio **8**:**9** = 85:15) and filtered. The off-white residue was washed three times with 10 mL benzene and dried in vacuo, yielding complex **9** as a white powder (30 mg; 10%). Colorless crystals of **9** suitable for X-ray crystallography were obtained from chloroform. The colorless filtrate was pumped to dryness and yielded complex **8** (90 mg; 61%). For **9**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 5.56 (s, $^1J_{PtP}$ = 1860 Hz, 2P), 6.83 (s, $^1J_{PtP}$ = 1734 Hz, 2P). ^1H NMR ($CDCl_3$): δ 6.0−8.0 (m, br, 42 H, Ar*H*), 4.4 (s, br, 1 H, CH_2P), 3.7 (s, br, 1 H, CH_2P), 3.5 (s, br, 4 H, CH_2P), 3.0 (s, br, 1

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H, CH_2P), 2.3 (s, br, 1 H, CH_2P), 1.7 (m, br, 6 H, 2-(CH_3)$_3$C$_6$HPt), 1.2 (m, br, 12 H, 4-6-(CH_3)$_3$C$_6$HPt), 0.8 (s, br, 6 H, PtCH_3) 0.4 (s, br, 6 H, PtCH_3).

Thermolysis of *trans*-[(DPPMH)PtCl$_2$]$_2$ (6). A solution of **6** (15 mg) in 0.6 mL of CD_2Cl_2 was loaded in a 5 mm screwcap NMR tube, heated to 140 °C overnight, and analyzed by $^{31}P\{^1H\}$ NMR, showing **7** as the major organometallic product (> 90%).

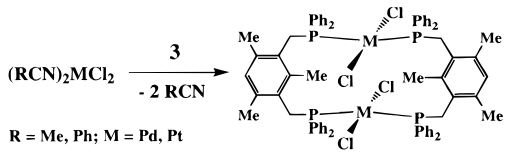
Heating of *cis*-(DPPMH)PtCl$_2$ (7) in the Presence of Excess MeCN. A solution of **7** (15 mg, 0.019 mmol) in 0.5 mL of CD_2Cl_2 and 0.1 mL of CD_3CN (1.9 mmol) was loaded in a 5 mm screwcap NMR tube, heated to 60 °C overnight, and analyzed by $^{31}P\{^1H\}$ NMR, showing **7** as the only organometallic product.

X-ray Crystal Structure Determination of *trans*-[(DPPMH)-PdCl$_2$]$_2$ (5). A yellow crystal (0.2 × 0.2 × 0.2 mm) was mounted on a glass fiber and flash frozen in a cold nitrogen stream (at 90 K) on a Rigaku AFC5R four-circle diffractometer mounted on a rotating anode with Mo Kα radiation and a graphite monochromator. Accurate unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections in the range $1.0° \le \theta \le 27.5°$. The SHELXS-86 and SHELX-76 program packages were used for structure solution and refinement.[11] Structure **5** was solved using automated Patterson analysis (SHELXS-86) and Fourier method (SHELX-76). The final cycle of the least-squares refinement gave an agreement factor R of 0.048 for all data. Two chloroform solvent molecules were also seen. Hydrogens were calculated from a difference Fourier map and refined with a temperature factor, $U_{over} = 0.042(2)$ Å$^2 \times 10^3$. An ORTEP view of the molecular structure and the adopted numbering scheme is shown in Figure 2. Tables 1 and 3 give details of the crystal structure determination. Selected bond angles and distances are listed in Table 3.

X-ray Crystal Structure Determination of *cis*-[(DPPMH)PtMe$_2$]$_2$ (9). A colorless transparent crystal (0.2 × 0.2 × 0.2 mm) was mounted on a glass fiber and flash frozen in a cold nitrogen stream (at 110 K) on a Rigaku AFC5R four-circle diffractometer mounted on a rotating anode with Mo Kα radiation and a graphite monochromator. Accurate unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections in the range $1.30° \le \theta \le 21.0°$. Data were collected to 21.0° ($d = 0.99$ Å) as diffraction was rather weak $\langle I \rangle / \sigma I = 7.2$. Data were not corrected for absoption effects as the crystal was frozen in a bead of oil so that the morphology was not measurable. The SHELXS-92 and SHELXL-93 program packages installed on a Silicon Graphics workstation were used for structure solution and refinement.[11] Structure **9** was solved using direct methods (SHELXS-92) and refined by full-matrix least-squares techniques based on F^2 (SHELXL-93). The final cycle of the least-squares refinement gave an agreement factor R of 0.0977 for data $I > 2\sigma$ (52% of the data). One chloroform molecule was also seen in occ. = 0.5. Hydrogens were calculated from the difference Fourier map and refined in a riding mode with individual temperature factors. An ORTEP view of the molecular structure and the adopted numbering scheme is shown in Figure 3. Tables 1 and 4 give details of the crystal structure determination. Selected bond angles and distances are listed in Table 4.

Results and Discussion

(a) Formation of Complexes 5−9. Displacement of the nitrile ligands from (RCN)$_2$MCl$_2$ (R = Ph or Me; M = Pd(II), Pt(II)) in THF or CH_2Cl_2 at room temperature by the aromatic bisphosphine **3** results in quantitative formation of the poorly soluble dimeric complexes *trans*-[(DPPMH)PdCl$_2$]$_2$ (**5**) and *trans*-[(DPPMH)PtCl$_2$]$_2$ (**6**) (eq 1).



5, M = Pd
6, M = Pt

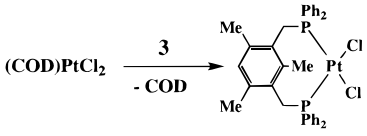
(1)

Table 1. Crystal data for Complexes **5** and **9**

	5	**9**
formula	$C_{70}H_{68}Cl_4P_4Pd_2 \cdot 2CHCl_3$	$C_{74}H_{80}P_4Pt_2 \cdot 0.5CHCl_3$
fw	1626.46	1543.12
space group	$P2_1/n$ (No. 14)	$P2_1/n$
cryst syst	monoclinic	monoclinic
a, Å	14.547(3)	19.187(4)
b, Å	17.431(4)	19.189(4)
c, Å	27.839(5)	20.705(2)
β, deg	99.56(2)	103.41(3)
V, Å^3	6961(3)	7415(3)
T, K	90	110
Z	4	4
D_{calcd}, g·cm^{-3}	1.522	1.382
μ(Mo Kα), mm^{-1}	1.035	3.947
cryst size, mm^3	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2
R^a	0.048	0.0977
$R_w{}^b$	0.049	0.2212

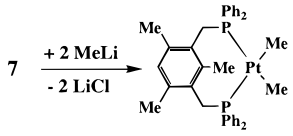
$^a R = [\sum| |F_o| - |F_c| |]/\sum |F_o|$. $^b R_w = [\sum_w(|F_o| - |F_c|)^2/\sum(w|F_o|^2)]^{1/2}$.

Displacement of COD from (COD)PtCl$_2$ by DPPMH (**3**) under similar reaction conditions as for reaction **1** results in the quantitative formation of the poorly soluble 8-membered monometallic complex *cis*-(DPPMH)PtCl$_2$ (**7**) (eq 2). Such complexes have been proposed as intermediates in C−H and C−C activation processes,[4] but were never observed directly.



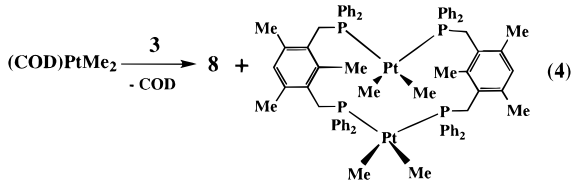
7 (2)

The dialkylplatinum(II) complex **8** is obtained in good yield (89%) by treating complex **7** with 2 equiv of MeLi (eq 3).



8 (3)

Reaction of **3** with (COD)PtMe$_2$ results in formation of a mixture (85:15) of the monomeric *cis*-(DPPMH)PtMe$_2$ (**8**) and the bimetallic *cis*-[(DPPMH)PtMe$_2$]$_2$ (**9**), which can be obtained spectroscopically pure by extracting complex **8** with benzene (eq 4). Such compounds (type **B**) are obtained by using specially designed substrates[8a] which have a preference for the *cis* orientation or are formed by using strongly directing ligands, as was also observed with platinum(II)-methyl complexes by Vrieze[12] and Puddephatt.[13]



9 (4)

(11) (a) Sheldrick, G. M. *SHELXS-92*, Program for crystal structure determination. University of Göttingen: Göttingen: Germany, 1992. (b) Sheldrick, G. M. *SHELXL-93*, Program for crystal structure refinement; University of Göttingen: Germany, 1993.

Table 2. Reactions of L_2MX_2 with **3**

compd	M	L_2	X	product	geometry	type	δ(P) ($^1J_{Pt,P}$) ($CDCl_3$, 25 °C)	Δ (ppm) δ(**5**−**9**) − δ(**3**)
5	Pd	2RCN[a]	Cl	dimer	trans	A	11.31	27.62
6	Pt	2RCN[a]	Cl	dimer	trans	A	8.49 (2526)	24.80
7	Pt	COD	Cl	monomer	cis	C	7.67 (3739)	23.98
8	Pt	COD	Me	monomer	cis	C	14.47 (1842)	30.78
9	Pt	COD	Me	dimer	cis	B	5.56 (1860)	21.78
							6.83 (1734)	23.14

[a] R = Me, Ph.

(b) Identification of Complexes 5−9. Complexes **5**−**9** were fully characterized using a combination of NMR (**5**−**9**), FAB-MS (**5**−**7**), FD-MS (**6**, **7**), X-ray (**5, 9**) (section c), and elemental analysis (**5**−**8**). ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR measurements showed broad lines. A variable temperature ^{1}H and ^{31}P{^{1}H} NMR study did not provide any conclusive answers on the nature of the line broadening, which could be a result of dynamic behavior, a slow tumbling rate of the molecules in solution (a common phenomenon for large molecules), or anisotropic effects. The experimental data are summarized in Table 2.

Complex **6** did not undergo any change upon mild heating (60 °C) in the presence of a 100-fold excesses of MeCN, suggesting that opening up of the disphosphine chelate is unlikely and does not contribute to the observed line broadening. Recording spectra at higher temperatures results in sharpening of the lines. In the ^{31}P{^{1}H} NMR of complexes **5**−**8** a single resonance appears, which is appropriate for a symmetric structure (Table 2). The resonances of the platinum complexes **6**−**9** are flanked by platinum satellites, allowing unambiguous determination of the geometry of these complexes based on the observed $^1J_{PtP}$. For complex **9** two broad resonances appear in a 1:1 ratio, probably due to the presence of two conformational isomers in solution. Similar observations were also reported by Shaw[14] and Hill,[7a] but the reason for this phenomenon is not clear. Puddephatt showed that a twisting motion of Pt(II) dimers can give unsymmetrical structures.[13a] The ^{1}H NMR is consistent with the ^{31}P{^{1}H} NMR and shows two sets of broad signals for the CH_2P and the PtMe groups. The aromatic methyl groups of **9** are significantly shifted to lower frequencies, which is likely a result of an anisotropic effect of the P-aryl rings.[17] The X-ray study of **9** shows indeed that the phenyl subsituents of the phosphines are in close range to the methyl groups (section c). The observed chemical shifts in the ^{31}P{^{1}H} NMR spectra are in the expected range for η^1-coordinated phosphine palladium(II) and platinum(II) complexes[15] and are hardly influenced by the metal (Pd or Pt) or the size of the macrocycle (8 versus 16 atoms). The observed relatively small $^1J_{PtP}$ = 2526 Hz for complex **6** indicates a P *trans* to P arrangement around the metal center, while the relatively large $^1J_{PtP}$ = 3739 Hz for complex **7** indicates a P *trans* to Cl orientation around the metal center.[15,16] The ^{31}P{^{1}H} NMR spectra of the platinum complexes **8** and **9** exhibit a relatively small $^1J_{PPt}$ coupling (≈1800 Hz),

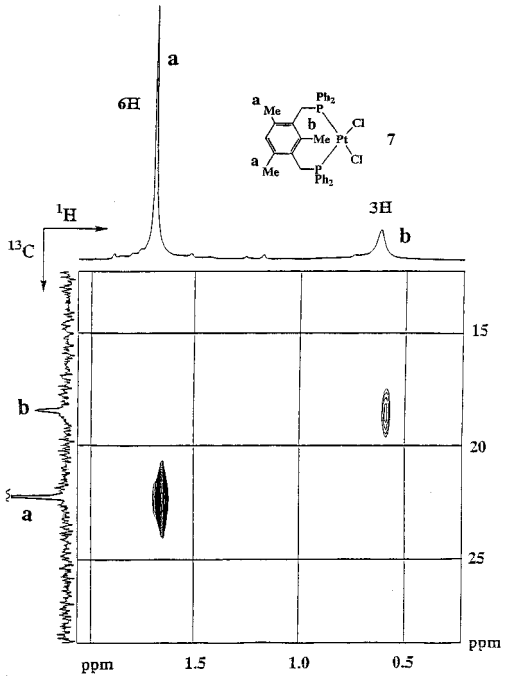


Figure 1. Part of a HMQC NMR spectrum of complex **7** in $CDCl_3$ at 313 K showing the correlation between the strongly shifted resonance in ^{1}H NMR (*X*-axis) and its not-shifted corresponding resonance in ^{13}C{^{1}H} NMR (*Y*-axis).

showing that the phosphine groups are positioned *trans* to the strong alkyl σ donors.[15] The 16-membered *trans* macrocycles **5** and **6** have similar spectroscopic properties. However, by NMR spectroscopy it is difficult to distinguish unequivocally between monomeric and dimeric structures except for the platinum complexes **6** and **7**, which are distinguishable by ^{1}H NMR. The mononuclear complex **7** exhibits in the ^{1}H NMR spectrum very broad resonances and a strongly shifted signal for one methyl group, which might be a result of an anisotropic effect,[17] as is observed for **9**. Significantly, the ^{13}C NMR shows no strongly shifted resonances (Figure 1) and the observed $^1J_{CH}$ = 125 Hz is fairly normal,[17] excluding the possibility of an agostic interaction.[18] The mononuclear complexes **7** and **8** exhibit similar NMR spectra, although in the ^{1}H NMR of complex **8** the shifted methyl group is partly overlapped with the broad resonances of the two Pt−Me moieties. FAB- and FD-MS of complexes **5**−**7** revealed the first solid evidence that we are dealing with mono- and dimeric structures, which is confirmed by X-ray crystallography of complexes **5** and **9** (section c).

(c) X-ray Crystal Structure Determination of 5 and 9. Single-crystal X-ray structures of complexes **5** and **9** unambiguously confirm the proposed bimetallic structures and the geometry around the metal centers. ORTEP views of the

(12) Kuyper, J.; van der Laan, R.; Jeanneaus, F.; Vrieze, K. *Transition Met. Chem.* **1976**, *1*, 199.
(13) (a) Puddephatt, R. J.; Thomson, M. A. *J. Chem. Soc.,Chem. Commun.* **1981**, 805. (b) Cooper, S. J.; Brown, M. P.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 1374.
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(15) (a) Pregosin, P. S. In *Phosphorous-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987. (b) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Complexes*; Springer: Berlin, 1979.
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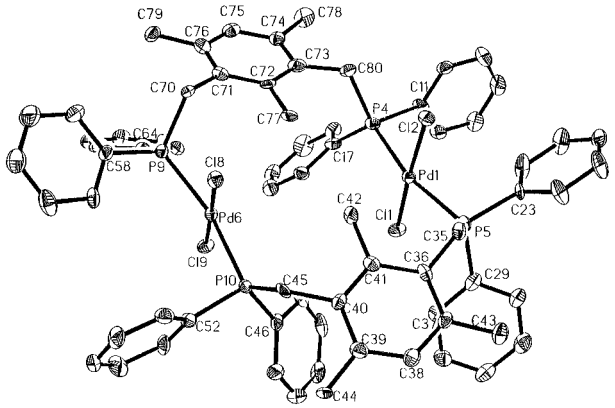

Figure 2. ORTEP view of complex **5**, showing that both ligands have adopted a *trans* arrangement around both metal centers.

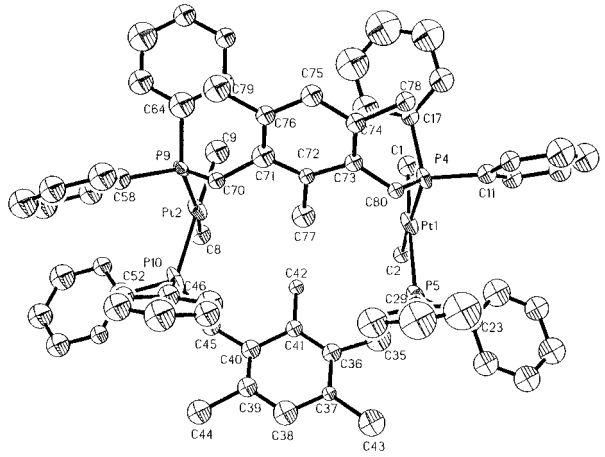

Figure 3. ORTEP view of complex **9**, showing that both ligands have adopted a *cis* arrangement around both metal centers.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **5** (Esd's in Parentheses)

Bond Lengths			
Pd(1)−P(4)	2.313(4)	Pd(6)−P(9)	2.313(4)
Pd(1)−P(5)	2.309(4)	Pd(6)−P(10)	2.319(4)
Pd(1)−Cl(1)	2.297(4)	Pd(6)−Cl(8)	2.322(4)
Pd(1)−Cl(2)	2.316(4)	Pd(6)−Cl(9)	2.290(4)
P(4)−C(80)	1.854(10)	P(5)−C(35)	1.847(10)
P(4)−C(17)	1.811(10)	P(5)−C(29)	1.796(10)
P(4)−C(11)	1.826(9)	P(5)−C(23)	1.826(9)
P(9)−C(70)	1.848(10)	P(10)−C(45)	1.868(11)
P(9)−C(64)	1.827(10)	P(10)−C(46)	1.824(10)
P(9)−C(58)	1.828(9)	P(10)−C(52)	1.829(9)
C(35)−C(36)	1.519(12)	C(45)−C(40)	1.497(12)
C(70)−C(71)	1.513(12)	C(80)−C(73)	1.514(13)

Bond Angles			
Cl(1)−Pd(1)−Cl(2)	175.8(1)	Cl(9)−Pd(6)−Cl(8)	178.4(1)
P(5)−Pd(1)−P(4)	165.0(1)	P(10)−Pd(6)−P(9)	166.8(1)
P(4)−Pd(1)−Cl(1)	89.2(2)	P(10)−Pd(6)−Cl(8)	90.7(2)
P(5)−Pd(1)−Cl(1)	86.6(2)	P(9)−Pd(6)−Cl(8)	87.3(2)
P(4)−Pd(1)−Cl(2)	90.4(2)	P(10)−Pd(6)−Cl(9)	88.9(2)
P(5)−Pd(1)−Cl(2)	92.7(2)	P(9)−Pd(6)−Cl(9)	92.8(2)
Pd(1)−P(4)−C(11)	98.6(4)	Pd(6)−P(9)−C(58)	107.7(4)
Pd(1)−P(4)−C(17)	117.4(4)	Pd(6)−P(9)−C(64)	118.9(4)
Pd(1)−P(4)−C(80)	120.5(4)	Pd(6)−P(10)−C(52)	97.4(4)
Pd(1)−P(5)−C(23)	104.2(4)	Pd(6)−P(10)−C(46)	119.5(4)
Pd(1)−P(5)−C(29)	119.8(4)	Pd(6)−P(9)−C(70)	113.2(4)
Pd(1)−P(5)−C(35)	115.5(4)	Pd(6)−P(10)−C(45)	120.0(4)
P(4)−C(80)−C(73)	118.4(7)	P(9)−C(70)−C(71)	117.2(7)
P(5)−C(35)−C(36)	115.7(7)	P(10)−C(45)−C(40)	118.4(7)

molecular structures and the adopted numbering schemes are shown in Figures 2 and 3. Tables 1, 3, and 4 give details of the crystal structure determination. Selected bond angles and distances are listed in Tables 3 and 4. The structures of **5** and **9** show neutral complexes in which the metal centers have an essentially square planar coordination geometry. The ligands (**3**) have adopted a similar arrangement around the two platinum (*cis*, *cis*) and palladium (*trans*, *trans*) centers. Any bonding interaction between the metal atoms in the solid state is clearly excluded by the magnitude of the intramolecular M···M separation (**5**, 5.971 Å; **9**, 6.401 Å). The units cells of **5** contains four molecules of **5** and eight molecules of $CHCl_3$; the unit cell of **9** contains four molecules of **9** and two molecules of $CHCl_3$, which was used as solvent for crystallization.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **9** (Esd's in Parentheses)

Bond Lengths			
Pt(1)−P(4)	2.300(8)	Pt(2)−P(9)	2.324(7)
Pt(1)−P(5)	2.319(9)	Pt(2)−P(10)	2.286(9)
Pt(1)−C(1)	2.12(3)	Pt(2)−C(8)	2.04(3)
Pt(1)−C(2)	2.09(2)	Pt(2)−C(9)	2.09(3)
P(4)−C(80)	1.89(2)	P(9)−C(70)	1.89(3)
P(4)−C(11)	1.82(2)	P(9)−C(58)	1.84(2)
P(4)−C(17)	1.85(2)	P(9)−C(64)	1.85(1)
P(5)−C(35)	1.86(3)	P(10)−C(45)	1.90(3)
P(5)−C(23)	1.88(2)	P(10)−C(52)	1.85(2)
P(5)−C(29)	1.88(2)	P(10)−C(46)	1.85(2)
C(35)−C(36)	1.56(4)	C(45)−C(40)	1.51(4)
C(70)−C(71)	1.48(3)	C(80)−C(73)	1.41(3)

Bond Angles			
C(2)−Pt(1)−C(1)	85.4(11)	C(8)−Pt(2)−C(9)	84.8(12)
C(2)−Pt(1)−P(4)	172.1(8)	C(8)−Pt(2)−P(10)	86.3(9)
C(1)−Pt(1)−P(4)	87.9(8)	C(9)−Pt(2)−P(10)	171.1(9)
C(2)−Pt(1)−P(5)	84.5(8)	C(8)−Pt(2)−P(9)	167.9(9)
C(1)−Pt(1)−P(5)	168.9(8)	C(9)−Pt(2)−P(9)	89.6(9)
P(4)−Pt(1)−P(5)	101.8(3)	P(10)−Pt(2)−P(9)	99.2(3)
Pt(1)−P(4)−C(17)	115.3(7)	Pt(2)−P(9)−C(64)	114.0(6)
Pt(1)−P(4)−C(11)	111.8(7)	Pt(2)−P(9)−C(58)	111.2(7)
Pt(1)−P(4)−C(80)	120.4(8)	Pt(2)−P(9)−C(70)	119.1(9)
Pt(1)−P(5)−C(29)	119.4(6)	Pt(2)−P(10)−C(46)	119.7(7)
Pt(1)−P(5)−C(23)	109.6(8)	Pt(2)−P(10)−C(52)	111.1(7)
Pt(1)−P(5)−C(35)	118.2(12)	Pt(2)−P(10)−C(45)	115.7(9)
C(71)−C(70)−P(9)	122(2)	C(36)−C(35)−P(5)	123(2)
C(73)−C(80)−P(4)	118(2)	C(40)−C(45)−P(10)	127(2)

First the structure of the palladium complex **5** will be discussed. The phosphines as well as the chloride ligands are in a *trans* arrangement. Whereas the Cl−Pd−Cl angles (175.8° and 178.4°) are close to linear, the P−Pd−P angles (165.0 and 166.8°) are significantly distorted. The Pd−P (2.309−2.319 Å) and the Pd−Cl (2.309−2.319 Å) bond distances are fairly normal.[19] The planarity of the coordination geometry around both palladium atoms has been determined by least-squares plane analysis through the atoms Pd(6), Cl(8), Cl(9), P(9), P(10) and Pd(1), Cl(1), Cl(2), P(4), P(5), which show relatively large mean deviations (0.1170 and 0.1135 Å, respectively) as a result of the acute P−Pd−P angles. The structure of the platinum complex **9** shows that the phosphines as well as the methyl groups are in a *cis* arrangement, as was concluded from the observed $^1J_{PPt}$ in $^{31}P\{^1H\}$ NMR (section b). The ligand arrangement for **9** is the one expected on electronic grounds, the strongest *trans* directors being situated mutually *cis*, which is unfavorable sterically. The steric influence is expressed by the relatively large P(4)−Pt(1)−P(5) (101.8°) and P(10)−Pt(2)−P(9) (99.2°) angles and the relatively small C(2)−Pt(1)−C(1) (85.4°) and C(8)−Pt(2)−C(9) (84.8°) angles. The Pt−P (2.286−2.324 Å) and Pt−C (2.04−2.12 Å) bond distances are in the range usually observed.[19] Four phenyl groups are in close range (3.606−4.067 Å) with four methyl groups (C(1), C(9), C(43), C(44)), which is also observed in the ^1H NMR (the

(19) Mathematical, Physical and Chemical Tables. *International Tables for Crystallography*: Wilson, A. T. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

resonances of the methyl protons are significantly shifted to lower frequencies; section b) The planarity of the coordination geometry around the platinum atoms has been determined by least-squares plane analysis through the atoms Pt(1), C(1), C(2), P(4), P(5) and Pt(2), C(9), C(8), P(9), P(10) which show relatively small mean deviations (0.0290 and 0.0892 Å, respectively). Thus, in the case of M = Pt and X = Me the electronically favorable but sterically hindered dimeric complex is formed as a minor product, while in the case of M = Pd and X = Cl the sterically favorable isomer is obtained quantitatively.

(d) Comments. Shaw obtained Rh, Pt, and Pd dimers with long-chain, flexible diphosphine ligands containing bulky, sterically demanding *tert*-Butyl substituents on the phosphorus atoms, while similar ligands with sterically less demanding phenyl substituents afforded open-chain products.[7b,c,14,20] The diphosphine ligand **3**, having phenyl substituents and a rigid backbone, reacts under mild reaction conditions to give Pt and Pd dimers. The loss of internal entropy upon coordination of **3** to a metal center is expected to be smaller due to the rigid backbone than that with an aliphatic hydrocarbon chain, enabling formation of dimers rather than open chain products.[14,20]

Importantly, only a monomeric complex (**7**) is formed in the reaction of DPPMH (**3**) with $(COD)PtCl_2$ (eq 2), indicating that this pathway is faster than the intermolecular reaction to afford **6**, which is formed quantitatively in the reaction of **3** with $(RCN)_2PtCl_2$ under similar reaction conditions (eq 1). Thermolysis of the dimeric *trans* complex **6** in CH_2Cl_2 at 140 °C results also in the formation of the thermally more stable monomeric *cis* complex **7**. The reason for the striking difference in product formation between $(COD)PtCl_2$ and $(RCN)_2PtCl_2$[21] is unclear, but this points out that, by choice of the neutral ligands (that are substituted by the phosphines), one can control the direction of the reaction. In the reaction of DPPMH (**3**) with $(COD)PtMe_2$ both a monomeric (**8**) and a dimeric complex (**9**) are formed (eq 4). The separated *cis* products (**8**, **9**) are stable in solution under the reaction conditions and are not in equilibrium with each other. Prolonged stirring of the reaction mixture did not change the product distribution, indicating that **8** and **9** are formed at comparable rates in parallel pathways. The origin of the difference in reactivity of $(COD)PtMe_2$ and $(COD)PtCl_2$ with the diphosphine PCP ligand, which is likely to be influenced by the higher methyl *trans* effect, needs further clarification.

(20) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856.

Conclusions

Our results show that product formation and distribution in the reactions of **3** with $(COD)PtX_2$ and with $(RCN)_2MCl_2$ are largely influenced by the nature of the metal precursor. The reactions of the aromatic diphosphine substrate DPPMH (**3**) with $(RCN)_2MCl_2$ (M = Pt, Pd) and $(COD)PtX_2$ (X = Cl, Me) precursors proceed in a highly regioselective manner. A remarkable change in coordination behavior of Pt(II) is observed by simply changing the neutral ligands. Metal precursors having nitrile ligands give exclusive formation of *trans* binuclear complexes **5** and **6**, while $(COD)PtCl_2$ gives exclusive formation of the *cis* mononuclear complex **7**. $(COD)PtMe_2$ give mixtures of both *cis* mono- and binuclear complexes **8** and **9**. Thermolysis of the sterically favorable *trans* bimetallic **6** results in the formation of the thermally more stable monometallic **7**. This process is undoubtedly driven by an increase in external entropy (assuming that solvation effects are small). Cyclometallation with PCP-type ligands **1** to obtain complexes such as **2** often requires heating,[1] perhaps to reverse the formation of bimetallic products such as **5**, **6**, and **9**.

Acknowledgment. We thank Han Peeters (University of Amsterdam) for performing the FAB- and FD-MS experiments, Dr. Leonid Konstantinovski for his help with the NMR experiments, and Hagit P. Affek for her technical assistance. The work was supported by the U.S.-Israel Binational Science Foundation, Jerusalem, Israel. D.M. is the holder of the Israel Matz Professorial Chair of Organic Chemistry.

Supporting Information Available: Text describing crystal structure analysis of **5**, tables listing of crystal data for **9** and bond distances and angles, anisotropic parameters, and hydrogen coordinates for **5** and **9**, and a figure showing an ORTEP diagram of **5** (13 pages). Ordering information is given on any current masthead page.

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(21) $(PhCN)_2MCl_2$ is known to have a *trans* configuration for M = Pd[9] and to be a *cis*/*trans* mixture for M = Pt, the *trans* isomer is thermodynamically more stable.[6]